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The spectra and structure of sulphur-containing organic compounds—IV. The vibrational spectra and conformations of haloidmethylmethylsulphones $CH_3SO_2CH_2X$*

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Abstract—The i.r. and Raman spectra of the haloidmethylmethylsulphones $CH_3SO_2CH_2Cl$ (**I**) and $CH_3SO_2CH_2Br$ (**II**) in their liquid, solution and crystalline states have been recorded. The presence of a mixture of *trans* and *gauche* conformations has been established. The temperature dependence of the i.r. spectra has been investigated and the value of $\Delta H = H(gauche) - H(trans)$ found. The band dichroism of the polarized i.r. spectra of crystalline **I** and **II** has been considered. The frequencies of the torsion vibrations have been found and the value of the internal rotation barrier measured. The interpretation of vibrational spectra is given and a normal coordinate analysis has been carried out.

INTRODUCTION

Data on internal rotation about the S–C bond in acyclic sulphoxides have been obtained earlier [1]. The relative stability of *trans* and *gauche* conformations is determined by the balance of various intramolecular interactions. To evaluate the contribution of these interactions to the total internal energy rotation one must obtain data on the conformations of molecules which differ only in the coordination of the sulphur atom and in the nature of the substituents of the S and C atoms.

It is intriguing to compare the characteristics of internal rotation about the S–C bond in sulphoxides and in compounds of the RSO_2CH_2X type. In Ref. [2] the vibrational spectra and conformations of the methanesulphonilchlorides $ClSO_2CH_2X$ (X = CH_3, Cl, Br) were studied. It was shown that a mixture of *trans* and *gauche* conformations was present in the liquid and solutions, with $\Delta H = 0 \pm 200$ cal/mol. Later the Raman spectra of a number of crystalline methanesulphonilchlorides were investigated [3]. The molecular structure of bromomethylsulphone $CH_3SO_2CH_2Br$ in the gas phase was investigated by the electron diffraction method [4]. Unfortunately, the authors assumed *a priori* that the molecules were in one conformation. Under this assumption all the molecules in the gas phase appeared to have the *gauche* conformation. A new analysis may be necessary, assuming the possibility of a mixture of conformations.

The present paper reports an investigation of the vibrational spectra and conformations of chloromethylmethylsulphone $CH_3SO_2CH_2Cl$ (**I**) and bromomethylmethylsulphone $CH_3SO_2CH_2Br$ (**II**).

EXPERIMENTAL

Infrared spectra in the range 400–4000 cm^{-1} were obtained on a Karl Zeiss UR-20 spectrometer. Raman spectra were obtained using a DFS-24 spectrometer equipped with a He–Ne laser. The experiment proceeded as in Refs [1] and [2]. Sulphones **I** and **II** were synthesized by literature methods [5]. Their spectra are presented in Figs 1–4.

RESULTS AND DISCUSSION

The study of dimethylsulphone by the electron diffraction method has shown that the molecules have a conformation in which the C–H bonds (CH_3 group) and the bonds at the S atom (S=O and S–C) are in the *gauche* orientation [6]. Therefore, it can be assumed that in the case of sulphones **I** and **II** two nonequivalent conformations are possible: with the *trans* and *gauche* orientations of the S–X and S–C bonds. The determination of the number of conformations in liquids and solutions is possible by comparison of the spectra of the liquids and crystals. In most cases molecules in the crystalline form exhibit only one

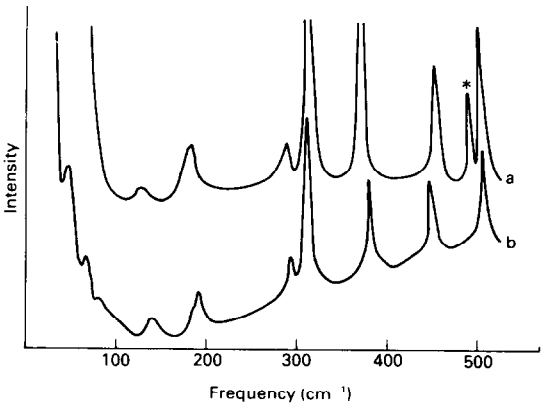

Fig. 1. Raman spectra of sulphone **I** (a, liquid; b, crystal).

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